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**CHEMICAL IONIZATION
ION CLUSTER MASS SPECTROMETRY**

by

Thomas C. Imeson
Charles S. Harden

May 1972



**DEPARTMENT OF THE ARMY
EDGEWOOD ARSENAL
Chemical Laboratory
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Thomas C. Imeson
Charles S. Harden

Physical Research Division

May 1972

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DEPARTMENT OF THE ARMY
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Chemical Laboratory
Edgewood Arsenal, Maryland 21010

FOREWORD

This report was authorized under Task 1W662710AD2901, Chemical Detection and Identification Technology, Detection and Identification Concepts. The report covers the period from June 1971 to December 1971.

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DIGEST

An extension of the technique of chemical ionization mass spectrometry utilizing moist N_2 or air as the reactant gas has been studied. Ionic clustering reactions involving protonated water clusters and trace quantities of organic impurities are initiated in a corona discharge at pressures ranging from 20 to 220 Torr. The ionic reaction products are analyzed with a quadrupole mass spectrometer. A mechanism is proposed for the formation of ions of the type $H^+(H_2O)_x(A)_y$ where A is the trace impurity. Results of detection studies on dimethyl methylphosphonate (concentration = 0.6 mole parts per million or $3.3 \mu g/l$) and dimethyl sulfoxide are reported.

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CHEMICAL IONIZATION ION CLUSTER MASS SPECTROMETRY

I. INTRODUCTION.

As interest mounts in the measurement of atmospheric contaminants and pollutants, as well as chemical agents, the detection and analysis of trace compounds present in the atmosphere or gas samples becomes increasingly important. A concomitance to this is the necessity to develop techniques for analysis that exhibit a broad applicability to many such substances. Mass spectrometry is recognized as an established and useful analytical technique for this purpose.¹⁻³ However, conventional ionization (EI) spectra from electron impact are difficult to utilize in trace analysis. Difficulties arise from the large number of fragment ions derived from each chemical constituent of the sample or, for gas chromatographic separation, the ever present problem of spectra interpretation and identification.⁴

The recent development of chemical ionization (CI) mass spectrometry⁵⁻⁹ has somewhat simplified the matter of trace compound analysis. This new technique relies on the mass analysis of ions representing products of ion-molecule reactions occurring within the ion source. As CI has been reported to date, the sample is introduced as a minor constituent in a reaction gas (a hydrocarbon such as methane) using a sample/reactant gas mole ratio between 1 to 100 and 1 to 1000 with the ion source operated at a pressure ca. 1 Torr. CI spectra obtained in this manner can be expected to have prominent high mass peaks and contain fewer fragment ion peaks than a comparable EI spectra.

Herein is reported a facet of the CI technique employing moist N₂ or air as the reactant gas. The reactant gas may be added to the sample or actually constitute the ambient atmosphere. Such an extension of CI is suggested by the recent discovery and subsequent study of proton ion/dipole clusters in the gas phase.¹⁰⁻¹³ Mechanisms, rate constants, and enthalpies of formation

¹Kiser, R. W. *Mass Spectrometry and Its Applications*. Chapter 9. Prentice-Hall, Englewood Cliffs, New Jersey, 1965.

²Dibeler, V. H. *Mass Spectrometry*. C. A. McDowell, Ed. pp 334-74. McGraw-Hill, New York, New York, 1963.

³Watson, J. T. *Ancillary Techniques of Gas Chromatography*. L. S. Ettre and W. H. McFadden, Ed. pp 145-225. Wiley, New York, New York, 1969.

⁴Biemann, K. *Mass Spectrometry*. p 170. McGraw-Hill, New York, New York, 1962.

⁵Munson, M.S.B., and Field, F. H. *Chemical Ionization Mass Spectrometry*. I. General Introduction. *J. Amer. Chem. Soc.*, **88**, 2621 (1966).

⁶Field, F. H. *Chemical Ionization Mass Spectrometry*. *Accounts Chem. Res.*, **1**, 42 (1968).

⁷Fales, H. M., Milline, G.W.A., and Nicholson, R. S. *Chemical Ionization Mass Spectrometry of Complex Molecules*. Esters of Di- and Tri-Carboxylic Acids. *Anal. Chem.*, **43**, 1785 (1971).

⁸Schoengold, D. M., and Munson, B. *Combination of Gas Chromatography and Chemical Ionization Mass Spectrometry*. *Anal. Chem.*, **42**, 1811 (1970).

⁹Apfenault, G. P., Dolhun, J. J., and Biemann, K. *Alternate or Simultaneous Electron Impact - Chemical Ionization Mass Spectrometry of Gas Chromatographic Effluent*. *Anal. Chem.*, **43**, 1720 (1971).

¹⁰Beckey, H. D. *Mass Spectrometric Investigation by Means of a Field-Emission Ion Source of Ion-Molecule Reactions and of the Association of Water*. *Z. Naturforsch.*, **15a**, 822 (1960).

¹¹Narcisi, R. S., and Bailey, A. D. *Mass Spectrometric Measurements of Positive Ions at Altitudes from 64 to 112 Kilometers*. *J. Geophys. Res.*, **70**, 3787 (1965).

¹²Shahin, M. M. *Use of Corona Discharges for the Study of Ion-Molecule Reactions*. *J. Chem. Phys.*, **47**, 4392 (1967).

¹³Good, A., Durden, D. A., and Kebabian, P. *Ion Molecule Reactions in Pure Nitrogen and Nitrogen Containing Traces of Water at Total Pressures of 0.5-4 Torr. Kinetics of Clustering Reactions Forming H⁺(H₂O)_n*. *J. Chem. Phys.*, **52**, 212 (1970), and *Mechanism and Rate Constants of Ion-Molecule Reactions Leading to Formation of H⁺(H₂O)_n in Moist Oxygen and Air*. *Ibid.*, p 222.

for ion clusters $H^+(H_2O)_n$ (derived from ion-molecule reactions initiated by the primary ions N_2^+ and O_2^+) have been established by Kebarle and his coworkers.¹³ For the technique of analysis being reported, the hydrated proton species serve as precursors for clusters $H^+(A)_n$ which represent the qualitative and quantitative indicators of the trace compound A.

II. EXPERIMENTATION.

Figure 1 is a schematic diagram of the apparatus which has been described in a previous report.¹⁴ Ions produced in a corona discharge or as products of ion-molecule reactions (formed at room temperature, $\sim 25^\circ C$) diffuse through a small pinhole into the vacuum chamber where they are focused into a quadrupole mass spectrometer. The mass spectrometer is a Varian residual gas analyzer (mass range: 0-250 amu) modified for use with this apparatus. Ion detection is accomplished with a Bendix magnetic electron multiplier coupled to a Keithly high-speed picoammeter.

Air or N_2 containing trace quantities of H_2O and the substance to be analyzed flow into the ion source - a corona discharge cylinder located at C (figure 1). The discharge is established between a 90% Pt-10% Rh wire, 0.003-inch diameter, and a stainless steel cylinder, 0.5-inch ID, located coaxial to one another. The discharge is started and maintained at 10 μA (for all source pressures) with a 10-kv variable power supply placed in series with a 4.7-m Ω current-limiting resistor. Ions exit the source chamber by diffusion through an orifice, 25- μ diameter, located in the center of S. Source pressures are varied to allow a control of the collision rate and the subsequent appearance and/or disappearance of particular ionic species of interest. Flow rate through the source is held constant for all pressures. For source pressures ranging from 1 Torr to 1 atm, the background pressure in the vacuum chamber varies between 10^{-7} and 10^{-5} Torr.

III. RESULTS AND DISCUSSION.

An example of a CI, ion-cluster, mass spectrum for dimethyl methylphosphonate (DMMP) is given in figure 2. The spectrum was taken using air as the reactant gas at a source pressure of 140 Torr, [DMMP] = .6 ppm (3.3 $\mu g/l$) and $[H_2O] \approx 10^{-4} \%$. Specific ionic species attributed to observed m/e are given in the table. Primary ions, N_2^+ and O_2^+ , as well as intermediate ion-molecule products do not appear in the spectrum beyond a source pressure of 20 Torr. Such a circumstance results from the ion-molecule reaction sequence, due to number of collisions involved, progressing to the extent that beyond 20 Torr only hydrated protons, and ion clusters subsequently formed, exist in the vicinity of the source exit. As can be seen in the table, indicators of the trace compound appear at m/e [MW + 1 + n(18)], e.g., $H^+(DMMP)(H_2O)_n$ and [n(MW) + 1], e.g., $H^+(DMMP)_n$ where n is 1 or 2. The mass range of the spectrometer precludes the observation of the cluster $H^+(DMMP)_3$ (m/e 373). However, evidence from other systems for which $H^+(A)_3$ is observed to be absent indicates that such a cluster does not exist.

Ions that appear under the category "other" in the table constitute background and can be attributed to clusters formed with methanol and acetone - solvents used in cleaning the apparatus. Consequently, no fragment ions need or can be assigned to the spectral elements. Efforts to remove or reduce this background do not succeed; however, the small contribution it makes, 3%, does not represent a problem.

¹⁴Harden, C. S. A Mechanism for the Formation of Electrically Charged Ammonia-Water Clusters in the Condensation Nuclei Personnel Detector. Edgewood Arsenal Technical Report, EATR 4569, Edgewood Arsenal, Maryland, November, 1971.

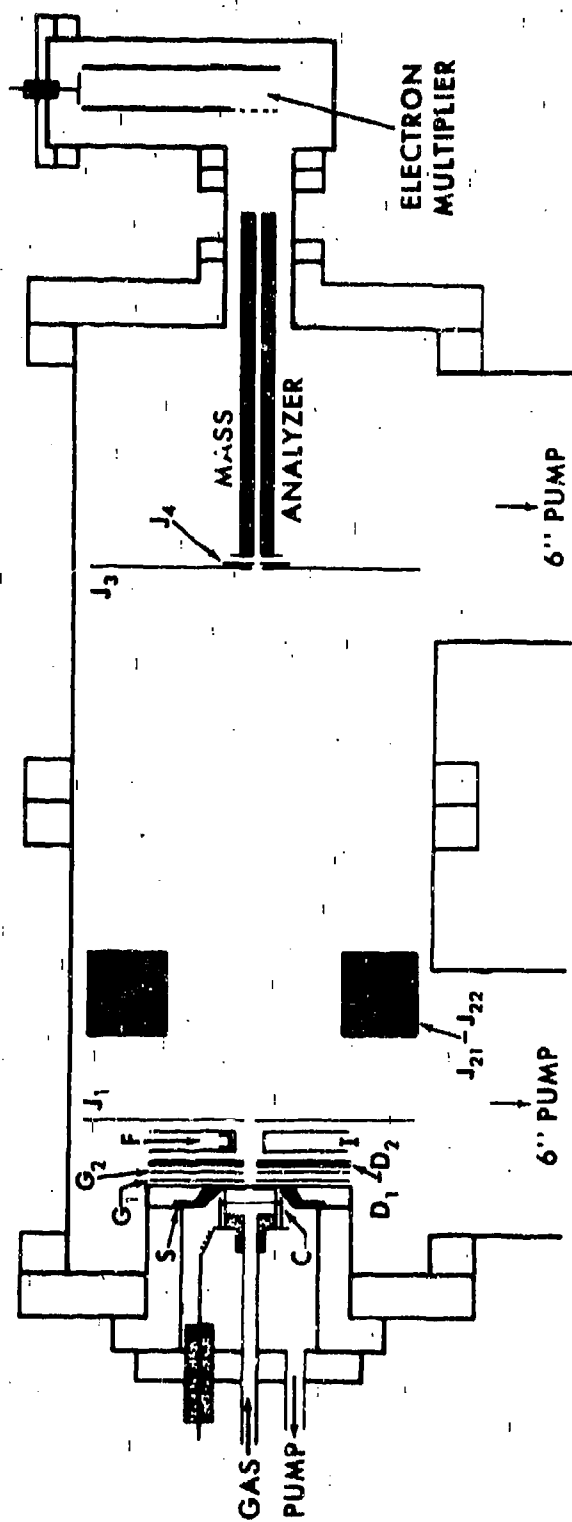


Figure 1. Schematic Diagram of CI, Ion Cluster, Mass Spectrometer

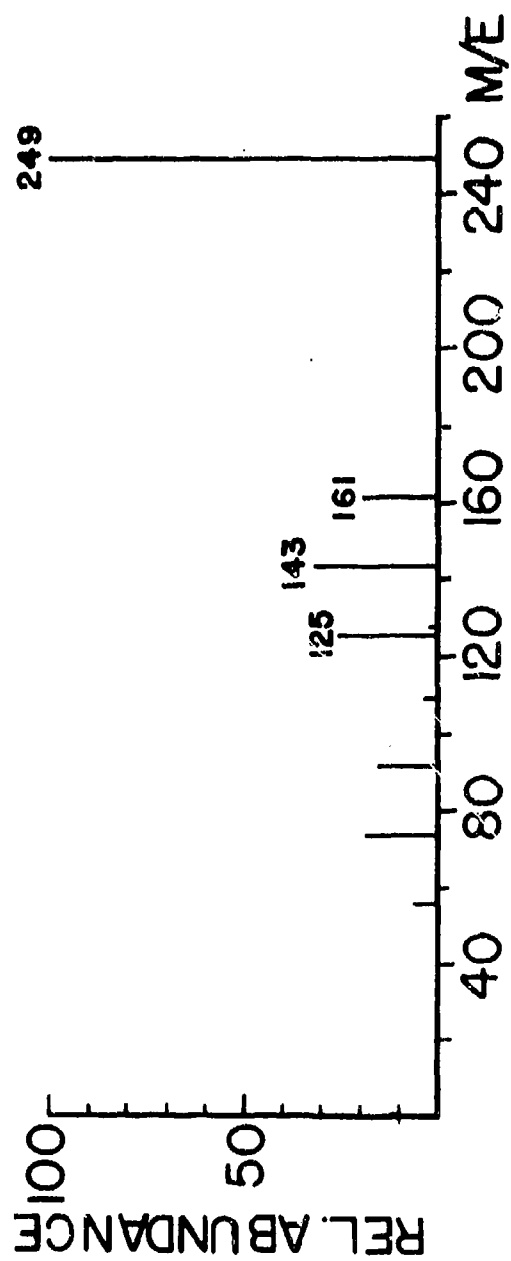
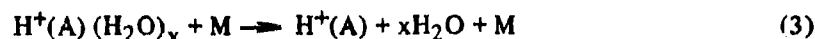
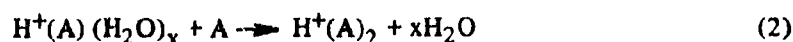
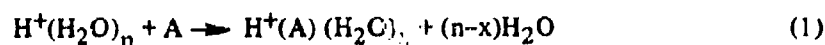


Figure 2. Ion Cluster Mass Spectrum of DMMP

Table. Identification of DMMP Spectral Elements

Ion	<i>m/e</i>	% I/Σ I
H ⁺ (H ₂ O) ₃	55	2.5
H ⁺ (H ₂ O) ₄	73	8.0
H ⁺ (H ₂ O) ₅	91	7.0
H ⁺ (H ₂ O) ₆	109	1.5
H ⁺ (DMMP)	125	11.1
H ⁺ (H ₂ O) ₇	127	1.0
H ⁺ (DMMP) (H ₂ O)	143	14.1
H ⁺ (DMMP) (H ₂ O) ₂	161	8.5
H ⁺ (DMMP) ₂	249	43.2
Other	-	3.1

Figure 3 illustrates the normalized ion intensity versus pressure relationship for the DMMP system in the pertinent high-pressure regions. Concentrations of DMMP and H₂O are the same as those indicated for the above spectrum (figure 2). Inspection of figure 3 suggests the following mechanism for trace compound ion cluster formation:



where $x = 1$ or 2 , n an integer $> x$, and M is a spectator molecule. Sequential appearance is justification for the first three steps of the mechanism. Reaction 4 is postulated for two reasons: (a) collision dynamics dictate that, as source pressure is increased, equilibrium will be achieved between $\text{H}^+(\text{A})$ and $\text{H}^+(\text{A})_2$, and (b) by analogy with the mechanism of $\text{H}^+(\text{H}_2\text{O})_n$ formation given by Kebarle¹³ as well as the proton ion cluster formation of benzyl acetate and *tert*-amyl acetate given by Field¹⁵. The existence of $\text{H}^+(\text{A})(\text{H}_2\text{O})_2$ is not a necessity in the above reaction sequence;

¹⁵Field, J. H. Chemical Ionization Mass Spectrometry. IX. Temperature and Pressure Studies with Benzyl Acetate and *tert*-Amyl Acetate. J. Amer. Chem. Soc., 91, 2827 (1969).

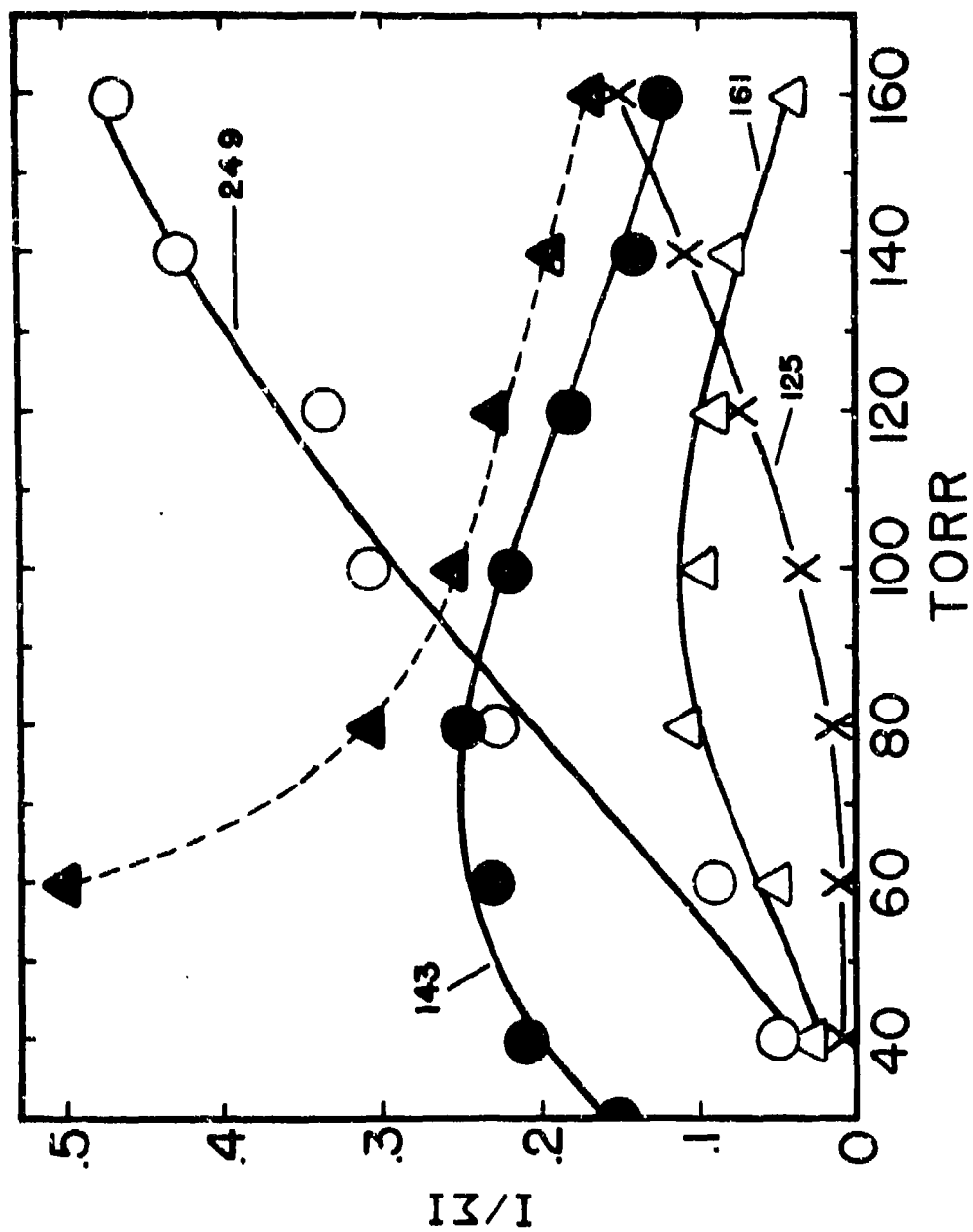


Figure 3. DMMP Clustergram; $[\text{DMMP}] = (3.3 \mu\text{g/l})$ $[\text{H}_2\text{O}] \approx 10^{-2}\%$.
 Curves Identified by m/e : \bullet , $\text{H}^+(\text{DMMP}) (\text{H}_2\text{O})$; \circ , $\text{H}^+(\text{DMMP})_2$;
 \times , $\text{H}^+(\text{DMMP})$; Δ , $\text{H}^+(\text{DMMP}) (\text{H}_2\text{O})_2$; \triangle , $\Sigma \text{H}^+(\text{H}_2\text{O})_n$

for it is observed to disappear, as the $[H_2O]$ is decreased, while leaving essentially the same relative intensity characteristics shown for other ion clusters in figure 3. Graphical representations such as figure 3 might be termed *clustergrams* after their counterparts in ΣI mass spectrometry which are called *clastograms*.

A clustergram for dimethyl sulfoxide (DMSO) is shown in figure 4. Concentrations and experimental parameters for DMSO are essentially the same as those used with DMMP. It will be noted that indicators of DMMP appear at lower pressures than those for DMSO and that the rate of formation of $H^+(DMSO)_2$ and $H^+(DMSO)$ are about the same. Without evidence to the contrary, the mechanism of formation of ion clusters for both DMMP and DMSO is assumed to be the same. However, for ion clusters formed from DMMP, reaction 2 has predominance over reaction 3, while for DMSO these two reactions have a parity in their probability of occurrence.

Dipole moments for DMMP¹⁶ and DMSO¹⁷ are respectively 3.62 and 3.96 Debye units; whereas their polarizabilities, computed from refractive indices, are 10.6 \AA^3 and 7.9 \AA^3 . An explanation for the apparent greater stability and ease of formation of clusters containing DMMP compared to DMSO may be interpreted as a greater influence of polarizability over dipole moment. However, the refractive indices and densities of the two substances are such that the difference in their polarizabilities is primarily a function of their molecular weights. Consequently, while dipole moment and polarizability certainly influence cluster formation, it is assumed that the greater number of vibrational degrees of freedom resident in the DMMP molecule impart a large stability to its clusters when compared to those of DMSO. This would seem to indicate that, within certain unspecified limits, the larger a dipolar molecule the more stable and readily formed will be its ion clusters. Further investigation is necessary to substantiate this prediction.

IV. CONCLUSIONS.

Irrespective of the nuances associated with ion cluster stability, the fact remains that the CI technique producing them offers an opportunity for application to the detection and analysis of trace compounds in the gas phase. The ability to use atmospheric gases as the reactant in CI considerably extends the utility of this technique. Its incorporation with gas chromatographic analysis of trace compounds (where N_2 is a common carrier gas) has many possibilities. Several features that enhance its general attractiveness are: (1) the absence of a spectrum complicated with fragment ions, (2) high mass peaks directly related to the molecular weight of the compound, and (3) sensitivity well below the ppm concentration range.

¹⁶ Kosolapoff, G. M. Dipole Moments of the Lower Dialkyl Alkylphosphonates. J. Chem. Soc. (London), 1954, 3222 (1954).

¹⁷ Nelson, R. D., Lide, D. R., and Maryott, A. A. Selected Values of Electric Dipole Moments for Molecules in the Gas Phase. NSRDS-NBS 10, US Government Printing Office, Washington, DC. 1967.

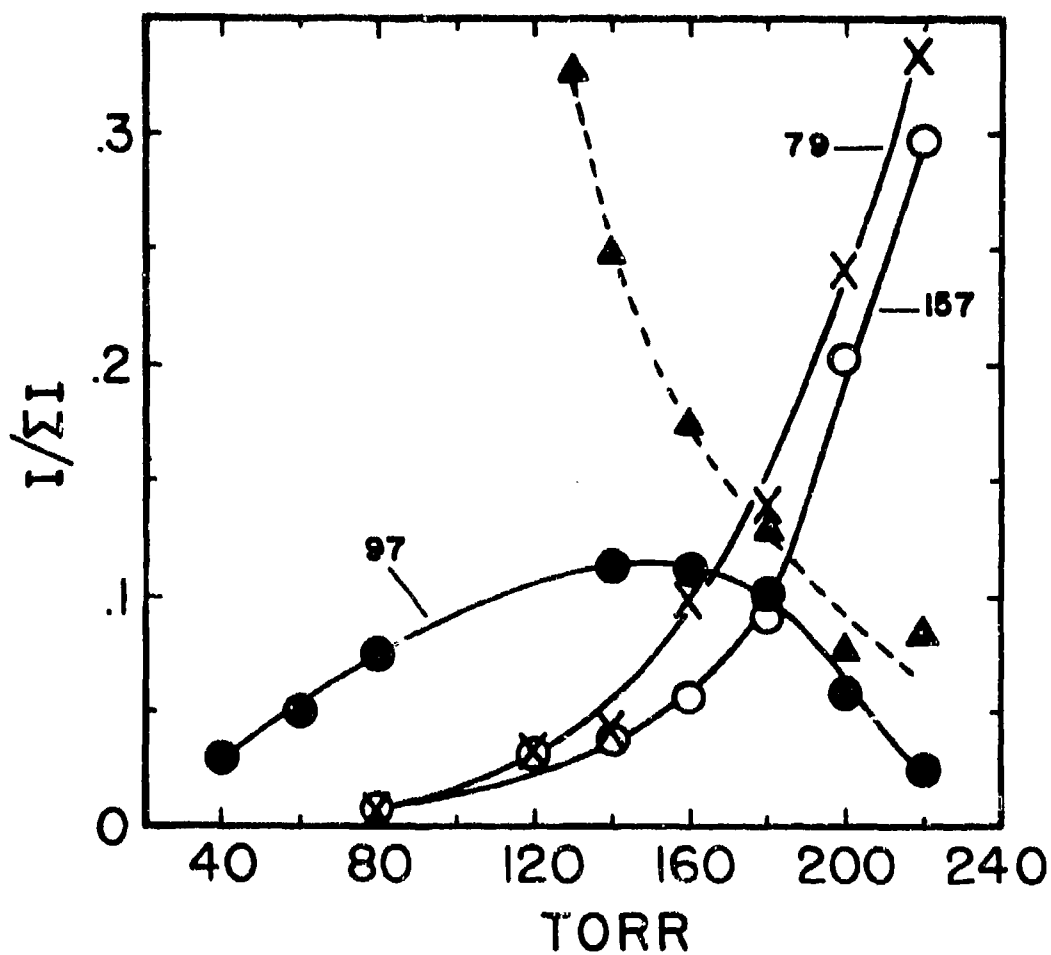


Figure 4. DMSO Clustergram; [DMSO] = .7 ppm, (2.4 $\mu\text{g/l}$) [H_2O] $\cong 10^{-2}\%$.

Curves identified by m/e ; \bullet , $\text{H}^+(\text{DMSO})(\text{H}_2\text{O})$; \circ , $\text{H}^+(\text{DMSO})_2$;
 \times , $\text{H}^+(\text{DMSO})$; \blacktriangle , $\Sigma \text{H}^+(\text{H}_2\text{O})_n$; $\text{H}^+(\text{DMSO})(\text{H}_2\text{O})_2$ not shown to facilitate clarity.

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